

# Molecular Dynamic Simulation of Liquid-Vapor Coexistence of Metals Modeled Using Modified Empirical Pair Potentials

**A. Sai Venkata Ramana**

Theoretical Physics Division, Bhabha Atomic Research Centre, Mumbai-400085, India

E-mail: [asaivenk@barc.gov.in](mailto:asaivenk@barc.gov.in)

**Abstract.** We performed Gibbs Ensemble Molecular Dynamics simulations to determine the Liquid-vapor coexistence curves of metals modeled with a modified form of inter-particle pair potential. The parameters of the potential are obtained by fitting the cold curve (Energy/atom Vs volume curve at  $0K$ ) obtained from the potential to that obtained from ab-initio calculations. Simulations are done for Aluminum, Copper, Sodium and Potassium and the results are analyzed. We find that the present results improve significantly over those obtained from Morse potentials (J.K. Singh et. al., Fluid Phase Equilibria 248(2006)).

## 1. Introduction

Equation of State(EOS) of materials for wide ranges of temperatures, pressures and densities is an essential requirement of hydrodynamic simulations which find applications in astrophysics, high energy density physics etc. First principles based density functional theory(DFT) calculations provide accurate description of thermodynamic properties of materials at zero temperature. However, to do a non-zero temperature calculation, particularly in the fluid regime, DFT has to be coupled with either Molecular Dynamics (MD) or Monte-Carlo (MC) methods. This enormously increases the computational cost and the method becomes impractical for large scale computations which are required for many practical purposes. Thus theoretical modeling of EOS of materials in the expansion phase based on classical statistical mechanical methods still plays a major role in generating thermodynamic data of materials. Basic input for theoretical modeling of EOS is the inter-particle interaction.

Presently, various forms of embedded atom model(EAM)[1, 2] potentials are available in the literature. However, a recent simulation study of liquid-vapor phase diagram using a particular form of EAM showed that the potential even though is good in predicting solid state properties, is not accurate enough in predicting the liquid vapor phase diagram [3]. Besides that, all the presently available theoretical models for EOS are restricted to pairwise inter-particle potentials. A way to obtain effective

pair potential from EAM potential has been developed by Foiles[4] based on Taylor series expansion of the embedding term around equilibrium solid density. However, the method is found to be working only for densities close to melting. Thus obtaining pair potentials which can predict accurately their thermodynamic properties for wide ranges of temperatures and pressures is an important requirement.

In the present paper, we emphasize on metals. Two model pair potentials have been widely used to describe the inter-particle interactions in metals. They are the generalized Lennard-Jones (GLJ) and the Morse potentials. The parameters of Morse potential for various cubic metals have been obtained by Lincoln et. al. [5] by using the Lattice parameter, bulk modulus and cohesive energy data. Lincoln et. al. have accounted for interaction between particles up to ninth neighbor shell in obtaining the parameters. J.K. Singh et. al. [6] have obtained the liquid-vapor phase diagrams for various metals using the Morse potential as parametrized by Lincoln et. al. from classical MD. Their results show that there is enormous deviation between the simulation and experimental values in the case of alkali metals although the results show a reasonable agreement with literature data in the case of Aluminum, Copper and Gold. On the other hand, there is a recent parametrization of the GLJ potential with some modification by Sun Jiuxun[7]. The author showed that Pressure Vs volume curve at 0K generated from this potential by taking only nearest neighbor interaction is in good agreement with experimental results. However, we observed that the energy Vs volume curve is not matching with the ab-initio data and the cohesive energy is highly erroneous in some cases[8]. Apart from this, the excess internal energy per particle calculated from the GLJ potential using parameters obtained by Sun Jiuxin is found to be diverging for most of the materials and classical molecular dynamics was not possible with that potential.

These problems might have arisen because of attempting to fit the potential with only two or three experimentally measured physical quantities like cohesive energy, bulk modulus and its pressure derivative, which are just equilibrium properties. The accuracy of the cold curve away from the equilibrium particularly in the expansion region is unknown. However, accuracy of the cold curve in the expansion region might play a role in determining the accuracy of the calculations of thermodynamic properties of corresponding fluid. On the other hand, accurate and fast DFT calculations of the cold curve are possible with the present day available codes. Thus we use the cold curve obtained from ab-initio calculations to obtain parameters of the potential. We fit the cold curve obtained from a given form of potential to that obtained from ab-initio data. This gives a clear idea of the accuracy of the parametrized cold curve form far from the equilibrium. When this procedure is done with Morse and GLJ potentials, we observed that the cold curves obtained from them are deviating from ab-initio data away from the equilibrium particularly in the case of alkali metals. Hence we propose a modified form of empirical potential which we expect to be accurate enough even far from the equilibrium for a wide class of metals.

Thus in the present paper, we describe an alternative way of obtaining parameters of empirical potentials and also a modified form of empirical potential. To test the

accuracy of the potentials so obtained, we obtained liquid vapor coexistence points for various temperatures for Aluminum, Copper, Sodium and Potassium using Gibbs ensemble molecular dynamics(GEMD) with the modified potential. In Section II, we describe the way we obtained parameters of the potentials using ab-initio data and the cold curves (Envergy Vs volume curves) from different potentials for various metals are compared and contrasted. In sec III, the GEMD method we adopted is explained in brief and liquid-vapor phase diagrams we obtained for Aluminum, Copper, Sodium and Potassium are shown and results are analyzed. The paper is concluded in Section IV.

## 2. Pair Potential Models for Metals

The GLJ potential is given by

$$u_{LJ}(r) = \frac{\epsilon}{m_1 - n_1} \left[ n_1 \left( \frac{r_0}{r} \right)^{m_1} - m_1 \left( \frac{r_0}{r} \right)^{n_1} \right] \quad (1)$$

Jiuxun[7] proposed a relation between  $m_1$  and  $n_1$  so that only one is independent. The relations are  $m_1 = 6n - 3$  and  $n_1 = 3n - 3$ . Taking his modification into account, the potential becomes,

$$u_{LJ}(r) = \frac{\epsilon}{3n} \left[ (3n - 3) \left( \frac{r_0}{r} \right)^{6n-3} - (6n - 3) \left( \frac{r_0}{r} \right)^{3n-3} \right] \quad (2)$$

In the present work we consider  $n$  as a parameter. The Morse potential is

$$u_M(r) = \epsilon(e^{-2\alpha(r-r_0)} - 2e^{-\alpha(r-r_0)}) \quad (3)$$

We propose a new form of pair potential given by

$$u_s(r) = \epsilon \left[ e^{-2\alpha(r/r_0-1)} \left( \frac{r_0}{r} \right)^{2\beta} - 2e^{-\alpha(r/r_0-1)} \left( \frac{r_0}{r} \right)^{\beta} \right] \quad (4)$$

Attractive part of the above potential is chosen inspired by the screening of ions by electrons in metals. Repulsive part is chosen ad-hoc as per mathematical convenience. It can be seen that by putting  $\beta = 0$  in above potential we recover the Morse potential and by putting  $\alpha = 0$ , it becomes a Lennard-Jones type potential. Since the electron-ion screening term is represented by an exponential term multiplied by the coulomb term (at-least in the semi-classical picture), we expect that a similar form with the exponents of the exponential and the  $r$  in the potential being adjusted, would represent the interactions in a better way. In the case of GLJ potential,  $r_0, n$  and  $\epsilon$  are the parameters. For the Morse potential,  $\epsilon, \alpha$  and  $r_0$  are parameters and for the modified potential,  $\epsilon, \alpha, \beta, r_0$  are the parameters. For all the potentials, the potential is minimum at  $r_0$  and the well depth is  $\epsilon$ .

### 2.1. Obtaining the Potential Parameters

We used Energy Vs volume data obtained from ab-initio calculations to obtain the parameters of the potentials. Ab-initio calculations were done using VASP[9] software. PAW potentials and Monkhorst-Pack grid in reciprocal space have been used. The

number of points in reciprocal space have been adjusted inspecting the convergence of the total energy for each case. Also, the energy of free atom has been calculated by taking a large volume per atom and has been subtracted from the total energy per particle so that cohesive energy can be calculated directly from the curve. The cold curve i.e., the zero Kelvin isotherm for each model potential is written as follows.

$$U = \sum_{i=1}^m \frac{\delta_i \epsilon}{2} u_x(a_i) \quad (5)$$

where  $x$  can be  $LJ, M$  or  $s$ .  $U$  is the energy per particle.  $a_i$  is the distance of the  $i^{th}$  neighbor from a particle situated at origin.  $\delta_i$  is the number of  $i^{th}$  neighbors. In the present work we have accounted interaction up to  $(m =) 10^{th}$  neighbor. Now  $a_i$  is related to volume per atom as follows:

In the case of a fcc solid,  $a_i = \sqrt{i}a_1$  and  $a_1 = a/\gamma$ . Where  $a$  is the lattice parameter and  $\gamma$  is the structural constant. For fcc solids, volume per atom  $V = a^3/4$  and  $\gamma$  is equal to  $\sqrt{2}$ . For simplicity, we write  $r_0$  as  $(4V_0)^{1/3}/\gamma$  without loss of generality. Thus using this information, Eq.(5) can be written in terms of volume per atom  $V$ . The equation then becomes

$$U = \sum_{i=1}^m \frac{\delta_i \epsilon}{2} u_x(V/V_0) \quad (6)$$

For example, using  $u_s(r)$  in  $U$ ,

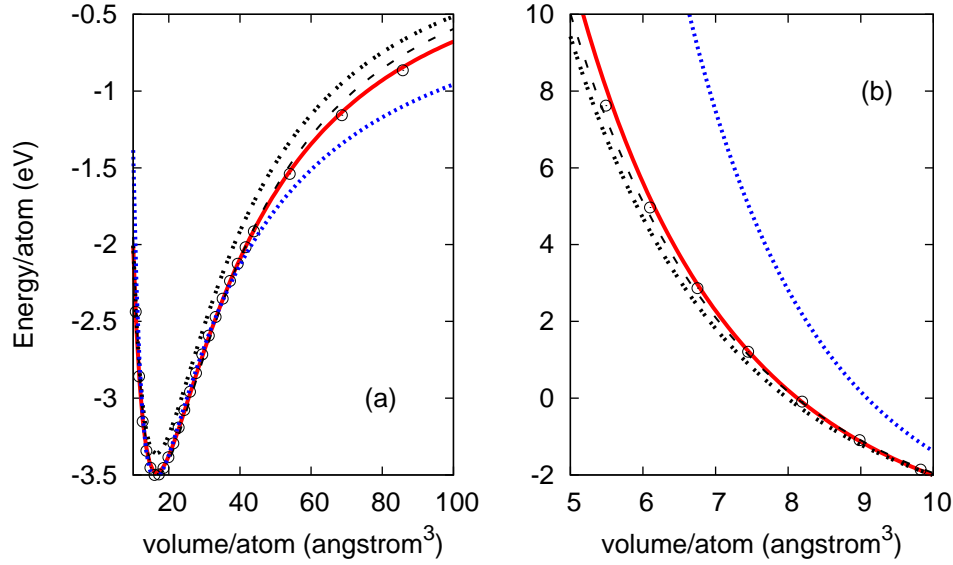
$$U = \sum_{i=1}^m \frac{\delta_i \epsilon}{2} \left[ \frac{e^{-2\alpha(\sqrt{i}(V/V_0)^{1/3}-1)}}{i^\beta} \left(\frac{V_0}{V}\right)^{2\beta/3} - 2 \frac{e^{-\alpha(\sqrt{i}(V/V_0)^{1/3}-1)}}{i^{\beta/2}} \left(\frac{V_0}{V}\right)^{\beta/3} \right] \quad (7)$$

In the case of a bcc solid,  $\gamma = 2/\sqrt{3}$  and  $V = a^3/2$ . However, the  $a_i$  do not hold a general relation with  $a$  as for fcc solids and have to be carefully calculated. In this case  $r_0$  is chosen as  $(2V_0)^{1/3}$ . Writing  $a_i = d_i a$  where  $d_i$  is to be calculated using the crystal structure, equation corresponding to  $u_s(r)$  is

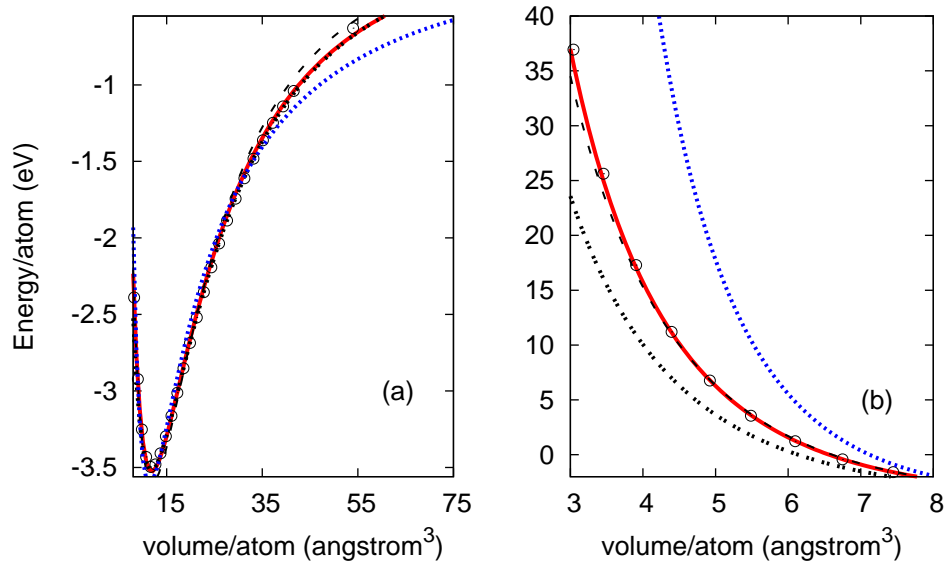
$$U = \sum_{i=1}^m \frac{\delta_i \epsilon}{2} \left[ \frac{e^{-2\alpha(d_i(V/V_0)^{1/3}-1)}}{d_i^{2\beta}} \left(\frac{V_0}{V}\right)^{2\beta/3} - 2 \frac{e^{-\alpha(d_i(V/V_0)^{1/3}-1)}}{d_i^\beta} \left(\frac{V_0}{V}\right)^{\beta/3} \right] \quad (8)$$

The parameters of the potential are obtained by fitting the cold curve Eq.(6) to the ab-initio cold curve.

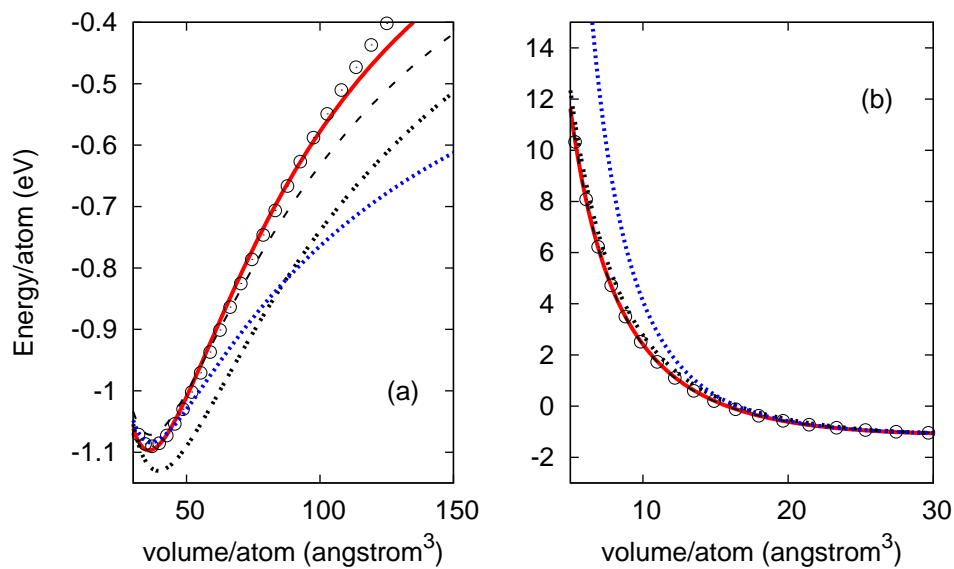
The fitted zero Kelvin isotherms obtained from various potentials for Aluminum, Copper, Sodium and Potassium are shown in Figs.(1-4). From the figures it can be seen that the cold curve from GLJ potential with Jiuxun's modification is quiet off from the ab-initio data away from the equilibrium in all the cases and in both compression and expansion phases. The cold curve obtained from Morse potential with parameters given by Lincoln et. al.(which we denote by  $U_{MLin}(V)$ ), in the case of Aluminum has slight deviation from ab-initio data near the equilibrium and away from equilibrium also as the cohesive energy predicted by ab-initio calculations and that used by Lincoln et. al. differed slightly. On the other hand, the cold curve from Morse potential fitted to the ab-initio data (denoted as  $U_M(V)$ ) and that from modified potential ( $U_s(V)$ ) had



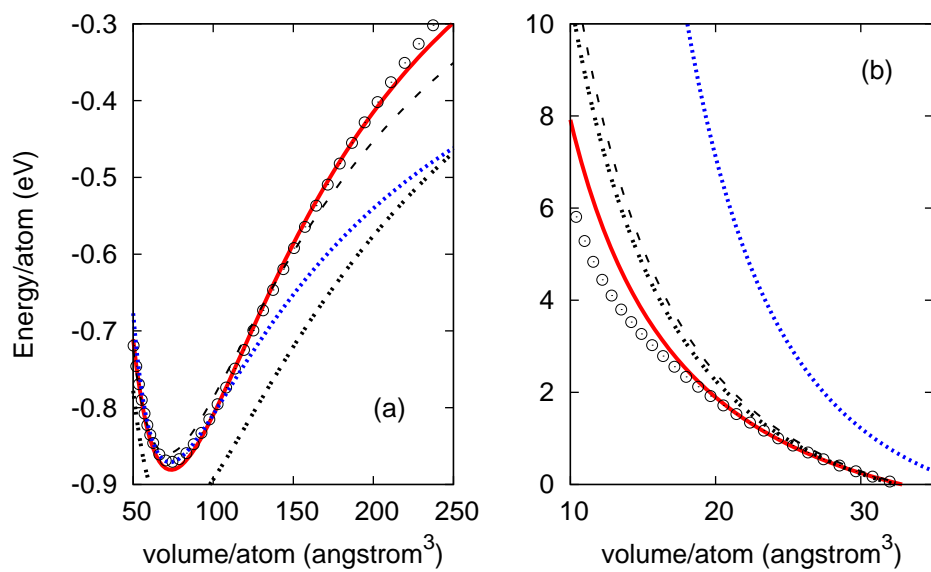
**Figure 1.** Zero Kelvin isotherm for Aluminum obtained using various potentials by fitting to ab-initio data. (Dotted Line: cold curve from GLJ potential), (Double dots: Cold curve from Morse potential parametrized by Lincoln et. al.[5]), (Dashes: Cold curve from Morse potential fitted to ab-initio data), (Solid line: Cold curve from modified potential), (circles: ab-initio data). Panel (a) is for expansion phase and panel (b) is for compression phase.



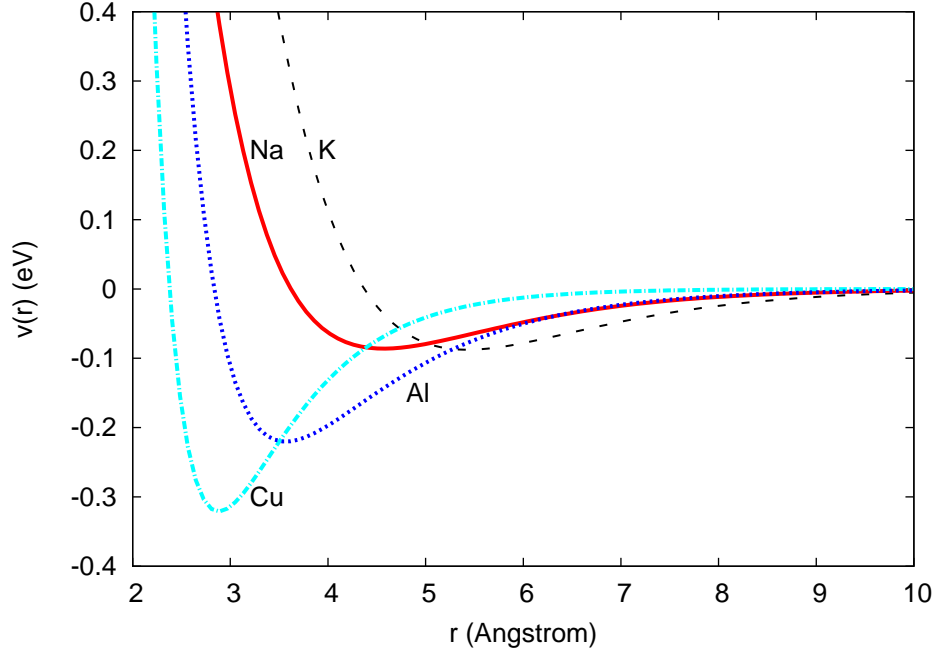
**Figure 2.** Zero Kelvin isotherm for Copper. Description same as in Fig.(1)



**Figure 3.** Zero Kelvin isotherm for Sodium. Description same as in Fig.(1)



**Figure 4.** Zero Kelvin isotherm for Potassium. Description same as in Fig.(1)



**Figure 5.** Modified pair potentials for Aluminum, Copper, Sodium and Potassium.

same accuracy except for a slight deviation of  $U_M(V)$  from the ab-initio data away from equilibrium in the expansion phase. In the case of Copper,  $U_{MLin}(V)$ ,  $U_M(V)$  and  $U_s(V)$  are equally accurate in the expansion phase. But in the compression phase,  $U_{MLin}(V)$  had a significant deviation from ab-initio data. For sodium and potassium, cold curves from ab-initio calculations and that given by  $U_{MLin}(V)$  are deviating significantly. This could be because of improved accuracy of the present ab-initio calculations in predicting the cohesive energies. Also, the  $U_M(V)$  deviated significantly from the ab-initio data in the expansion region far from the equilibrium for both sodium and potassium. Whereas in the compression region,  $U_M(V)$  is matching reasonably well with ab-initio data for Sodium and is deviating from ab-initio data for Potassium. On the other hand,  $U_s(V)$  matched with reasonably well with ab-initio cold curve in both the cases.

From the above discussion,  $U_s(V)$  obtained from  $u_s(r)$  matched with the ab-initio cold curve better than those obtained with other potentials for all the cases shown far away from equilibrium, particularly in the expansion region. Of course, it has to be noted  $U_M(V)$  is accurate enough for Aluminum and Copper. Thus we expect that the potential  $u_s(r)$  may give an improved description of the metals in the liquid region.  $u_s(r)$  for Aluminum, Copper, Sodium and potassium is shown in Fig.(5) Parameters for the potential  $u_s(r)$  obtained using the procedure described above are listed in Table.1. It can be seen that for Sodium and Potassium, the parameter  $\beta$  becomes negative which will make the potential turn down and go to zero close to origin which is unphysical. Thus it has to be cutoff at an appropriate point close to the origin. We found that  $0.25r_0$  and  $0.4r_0$  can be the cut-off points for Sodium and Potassium respectively. It is assumed that for distances smaller than these, the potential is kept constant and equal to that at

**Table 1.** Parameters for  $u_s(r)$ 

metal	$\epsilon(eV)$	$r_0(A^o)$	$\alpha$	$\beta$
Al	0.220	3.568	2.499	0.7808
Cu	0.321	2.881	3.095	0.792
Na	0.086	4.567	3.968	-0.5573
K	0.088	5.425	5.172	-1.439

the cutoff point. Clearly, this would not effect the results as the probability of finding an atom inside the repulsive core is negligible. In order to test the accuracy of modified potential  $u_s(r)$  in the fluid phase, we obtained liquid-vapor phase diagrams(LVPDs) for all these metals using Gibbs ensemble molecular dynamics.

### 3. Liquid-Vapor Phase Equilibria

We use GEMD([10]-[15]) method to obtain the liquid-Vapor phase coexistence curves. The basic idea of GEMD is to simulate the conditions of liquid-vapor coexistence. The system contains two simulation boxes. Total number of particles in the system is kept constant. However, exchange of particles between boxes is allowed. One box is assumed to be situated in an infinite medium of homogeneous liquid at a (given) constant temperature and the other is assumed to be situated in an infinite medium of homogeneous vapor at the same temperature. Since the idea is to get the thermodynamic properties of a macroscopic system, the interface effects are neglected. The coexistence conditions are simulated by evolving the boxes in such a way that they have same temperature, pressure and chemical potential after equilibration as required by the Gibbs phase rule. Initially, each box is given a guess density(i.e., no. of particles and volume). Equilibration would be faster if the guess densities are closer to the coexisting liquid and vapor densities. Periodic boundary conditions are applied to each box to ensure that they represent the bulk coexisting phases. Temperature fluctuations in each box are controlled by a Berendsen thermostat [16] so that they reach the given temperature. Pressures in both the boxes are equalized by controlling the volume fluctuations using a Berendsen barostat. This is done by adjusting the volume of each box such that the instantaneous pressure in one box becomes equal to the instantaneous pressure in the other. However the total volume of the two boxes is not restricted to be constant. The particle transfer step to equilibrate the chemical potential in both boxes is carried out after each five hundred time steps by comparing their chemical potentials. It is done as follows: A particle is chosen randomly from the box where chemical potential is more and is removed from it. Correspondingly a particle is introduced into the other with its potential energy calculated and the velocity taken from the Boltzmann distribution of corresponding temperature. However, care is taken so that the introduced particle is not too close to any other particle in the box. With the above three procedures being done during the simulation, the two boxes evolve in time in such away that they have same



temperature, pressure and the chemical potential after equilibration. Thus the system may phase separate into liquid in one box and gas in the other with proper choices of initial densities if the temperature of the system is less than the critical temperature. The method described above has been tested for the Lennard-Jones fluid initially. The phase diagram obtained matched with that of the earlier simulations[10] validating the code we developed. Then the code is used to obtain the LVPDs for the metals described above. Time step used for the simulations is 1 femto second and each simulation run has typically  $5 \times 10^5$  equilibration and production steps. The chemical potential has been evaluated using Widom's test particle insertion method[17]. In each step 200 test particles are inserted and the chemical potential is calculated after each five hundred steps. Total number of particles used in the simulation are 1728. The initial densities have been chosen so that after equilibration, both the boxes contain a good number of particles (few hundreds) so that the averages are reliable and deviations are small.

### *3.1. Results and Discussion*

The Temperature( $T$ ) Versus Density( $\rho$ ) diagrams for Aluminum, Copper, Sodium and Potassium are shown in fig.(6). The critical temperature( $T_c$ ) and critical density ( $\rho_c$ ) are obtained by fitting the simulation data using the law of rectilinear diameters

$$\frac{\rho_l + \rho_v}{2} = \rho_c + A(T - T_c) \quad (9)$$

and the power law

$$\rho_l - \rho_v = B(T - T_c)^\beta \quad (10)$$

where  $\rho_l$  and  $\rho_v$  are liquid and vapor densities.  $A$  and  $B$  are fitting constants and  $\beta = 0.33$ .

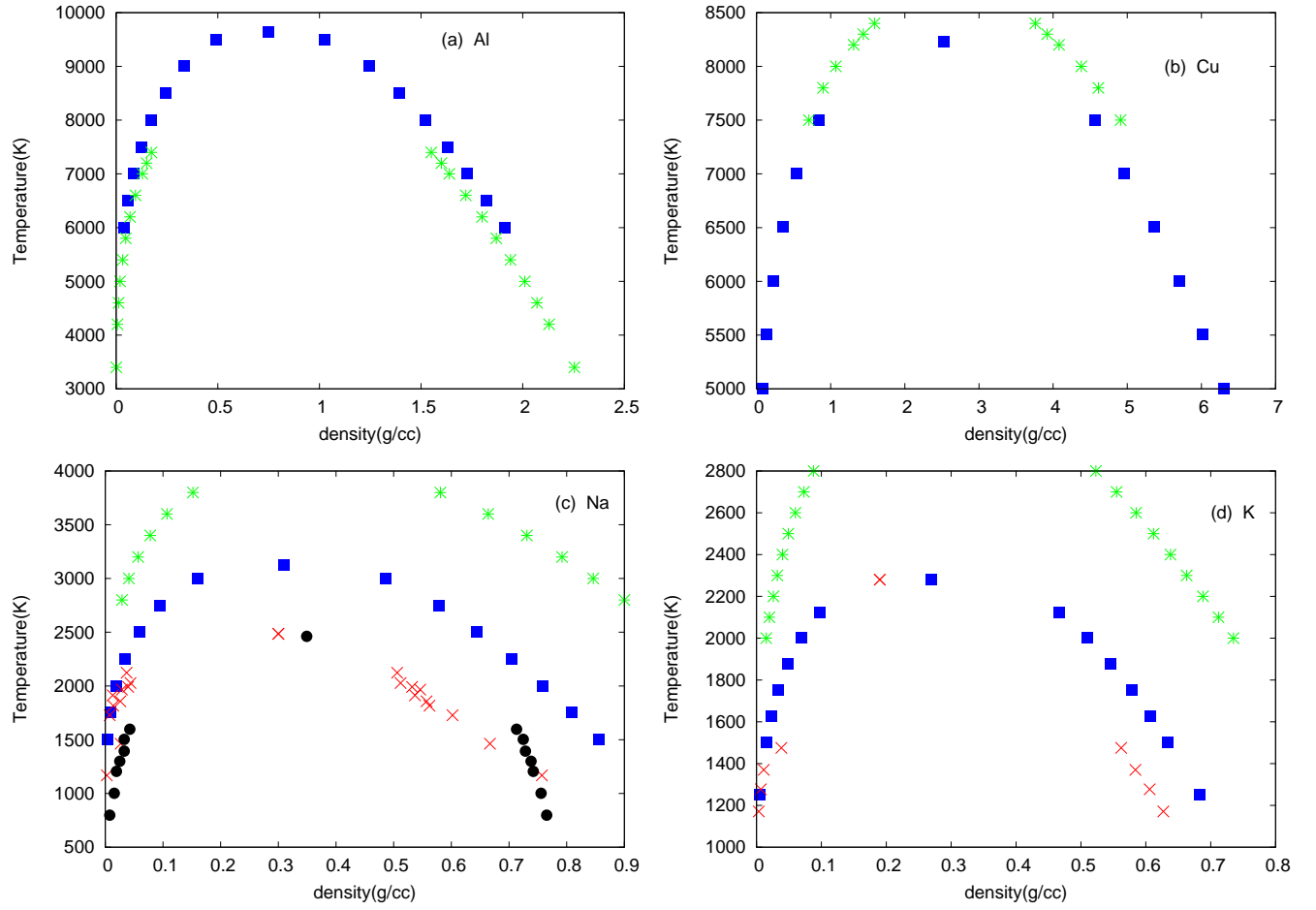
Critical parameters that we obtained are compared with literature data and experiments in Table.(II). In the case of Aluminum, the  $T_c$  and  $P_c$  we obtained are higher than the literature data. Whereas for copper our data is closer to the experimental value than that of Ref.[6] and Ref.[23]. On the other hand, in the case of Sodium and Potassium, our results are significantly improved over those obtained from Morse potential[6]. Also, experimental coexistence points are shown in Fig.(6c) and Fig.(6d) for Sodium and Potassium respectively. The figures clearly show a significant improvement over the earlier results using Morse potential throughout the phase diagram. However, still there is some deviation between our results and experimental coexistence points. In the case of Sodium, the coexistence points obtained by Singh et. al.[26] using EAM potential are closer to the experimental points at low temperatures. However, the asymmetry in experimental phase coexistence curve is not present in that obtained by Singh et. al. particularly in the liquid part of the coexistence curve. Whereas the asymmetry of the experimental curve is qualitatively maintained by that we obtained in this work.

**Table 2.** Critical Point Data

metal	$T_c(K)$	$\rho_c(g/cc)$	$P_c(GPa)$	Reference
Al	9643	0.75	0.81	This work
	7963	0.44	0.35	Faussurier[19]
	8860	0.28	0.31	Likalter[20]
	8387	0.38	0.45	Vinayak[21]
	8472	0.79	0.51	J.K. Singh[6]
Cu	8231	2.05	0.73	This work
	5696	1.8	0.11	Aleksandrov[23]
	8650	2.6	0.95	J.K. Singh[6]
	7696	1.93	0.58	Experiment[24]
Na	3121	0.31	0.109	This work
	2485	0.30	0.025	Experiment[25]
	3932	0.35	0.129	J.K. Singh[6]
	2462	0.35	0.011	J.K. Singh[26]
K	2280	0.27	0.037	This work
	2280	0.19	0.016	Experiment[25]
	3120	0.28	0.053	J.K. Singh[6]

#### 4. Conclusion

We proposed a modified form of empirical pair potential for metals and suggested a simpler way of obtaining parameters of the potential using the ab-initio cold curve. We noted that the cold curve obtained from the modified potential is accurate enough far from the equilibrium region for all the metals we worked with in the paper. We obtained liquid-vapor phase coexistence curves with the potential using GEMD and noted that there is a significant improvement in the phase diagrams over those obtained from Morse potential parametrized using equilibrium data. However, we find that still there is some deviation from the experimental results in the case of alkali metals. The deviation could be artifact of many body effects which cannot be accurately accounted within the pair potential formalism.



**Figure 6.** Liquid Vapor Coexistence Curves. (filled squares: Present work), (stars: J.K. Singh et. al. [6]), (Filled circles: J.K. Singh et. al. [26] ), (Crosses: Experiments [27]). (a)Aluminum, (b) Copper, (c) Sodium and (d) Potassium.

## 5. Acknowledgements

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## References

- [1] M. S. Daw and M. I. Baskes, Phys. Rev. B 29, 6443 (1984); Phys. Rev. Lett. 50, 1285 (1983).
- [2] M. S. Daw, S. M. Foiles and M. I. Baskes, Materials Science Reports 9, 251 (1993) and references therein.
- [3] A. Sai Venkata Ramana, J. Phys. : Conf. Series 377, 012086 (2012)
- [4] S. M. Foiles, Phys. Rev. B. 32, 3409 (1985)
- [5] R. C. Lincoln, K. M. Koliwad and P. B. Ghate, Phys. Rev. 157, 463(1967)
- [6] Jayant K. Singh , Jhumpa Adhikari , Sang Kyu Kwak, Fluid Phase Equilibria 246, 1 (2006)
- [7] Sun Jiuxun, J. Phys.: Condens. Matter 17, L103 (2005)
- [8] A. Sai Venkata Ramana, paper submitted to J.Phys: Condens. Matter

- [9] G. Kresse; J. Hafner, Phys. Rev. B 47, 558 (1993), G. Kresse, Furthmuller, J. Computat Mater Sci 6, 15(1996), G. Kresse, Furthmuller, Phys. Rev. B 54, 11 169(1996), G. Kresse, D. Joubert, Phys Rev B 59, 1758(1999)
- [10] A. Z. Panagiotopoulos; N. Quirke; M. Stapleton; D. J. Tildesley Mol. Phys. 63, 527 (1988)
- [11] M. J. Kotelyanskii and R. Hentschke Phys. Rev. E 51, 5116 (1995).
- [12] Bruce J. Palmer and Chaomei Lo J. Chem Phys. 101, 10899(1994).
- [13] Andras Baranyai and Peter T. Cummings Mol. Sim. 17, 21 (1996).
- [14] Christoph Bratschi and Hanspeter Huber J. Chem Phys. 126, 164104 (2007).
- [15] Wen-Ze Ou-Yang, Zhong-Yuan Lu, Tong-Fei Shi, Zhao-Yan Sun, and Li-Jia An J. Chem. Phys. 123, 234502(2005)
- [16] H. J. C. Berendsen, J. P. M. Postma, W. F. van Gunsteren, A. DiNola, and J. R. Haak J. Chem. Phys. 81, 3684 (1984)
- [17] B. Widom J. Chem. Phys. 39, 2803(1963)
- [18] Howard E. Alper, Peter Politzer Int. J. Quantum Chem. 76, 670(2000)
- [19] Gerald Faussurier, Christophe Blancard, and Pier Luigi Silvestrelli, Phys. Rev. B 79, 134202(2009)
- [20] A. A. Likalter, Physica A 311, 137 (2002)
- [21] Vinayak Mishra, S. Chaturvedi, Physica B 407, 2533 (2012)
- [22] Divesh Bhatt, Ahren W. Jasper, Nathan E. Schultz, J. Ilja Siepmann and Donald G. Truhlar J. Am. Chem. Soc. 128, 4224 (2006)
- [23] T. Aleksandrov, C. Desgranges, J. Delhommelle Fluid Phase Equilibria 287, 79 (2010)
- [24] H. Hess, Z. Metallkd, 89, 388(1998)
- [25] R. W. Ohse, J. F. Babelot, J. Magill, M. Tenenbaum, Pure & Appl. Chem. 57, 1407(1985)
- [26] A. K. Meya, Abhiram Hens, J. K. Singh, Fluid Phase Equilibria 16, 313(2012)
- [27] I. G. Dillon, P. A. Nelson, B. S. Swanson, J. Chem. Phys. 44, 4229(1966)